

<p>2001-019165/03 A25 E19 (A60) KAGA- 1999.03.09  ZH KAGAKU GIJUTSU SENRYAKU SUISHIN KIKO *JP 2000256457-A  1999.03.09 1999-061615(+1999JP-061615) (2000.09.19) C08G 65/12  <b>Composition for polymerization catalyst for propylene oxide for urethane material, contains a crown ether compound, an alkali metal alkoxide, or an alkali metal hydroxide and organic Lewis acid</b>  <b>C2001-005697</b></p>	<p>A(2-A, 2-A7, 5-G3, 5-H4) E(5-A, 5-B1, 6-A2E, 6-A3, 7-A4, 33-A3)</p> <p>The composition is used in the polymerization catalyst for producing the propylene oxide used in producing the poly(propylene oxide). The poly(propylene oxide) is used in an urethane material, resin material, surface active agent material.</p>
<p><b>NOVELTY</b>  A composition for polymerization for catalyst for a propylene oxide contains a crown ether compound, an alkali metal alkoxide, or an alkali metal hydroxide and organic Lewis acid.</p> <p><b>DETAILED DESCRIPTION</b>  A composition for polymerization for catalyst for a propylene oxide contains:  (a) a crown ether compound;  (b) an alkali metal alkoxide, or an alkali metal hydroxide; and  (c) organic Lewis acid in which all bonds are bonds formed by bonding carbon to a metal without oxygen.</p> <p><b>USE</b></p>	<p><b>ADVANTAGE</b>  The method produces the poly(propylene oxide) having a comparatively high molecular weight and a hydroxyl group at its terminal.</p> <p><b>TECHNOLOGY FOCUS</b>  Organic Chemistry - Preferred Crown Ether: The content of the crown ether compound is 1 mol or more per mol of the alkali metal alkoxide or the alkali metal hydroxide.  The crown ether compound consists of one or two or more selected from the group consisting of 18-crown-6, benzo 18-crown-6, dibenzo 18-crown-6, and dicyclohexano 18-crown-6.  Preferred Organic Lewis Acid: The organic Lewis acid is selected from alkyl aluminum, aryl aluminum, and/or alkyl aryl aluminum.</p> <p>JP 2000256457-A+</p>

<p>The production of a poly(propylene oxide) comprises:  (a) obtaining the poly(propylene oxide) obtained by polymerizing the propylene oxide;  (b) using the composition for the polymerization catalyst.  (4pp215DwgNo.0/0)</p>	<p>JP 2000256457-A</p>
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## PATENT ABSTRACTS OF JAPAN

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INSTITUTE(22)Date of filing : 09.03.1999 (72)Inventor : ISHIDA TOYOHISA  
ENDO TAKESHI(54) PROPYLENE OXIDE POLYMERIZATION CATALYST COMPOSITION AND PREPARATION OF  
POLY(PROPYLENE OXIDE)

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a propylene oxide polymerization catalyst composition capable of controlling the molecular weight of polymers and also forming a poly(propylene oxide) having hydroxyl groups at its terminals with a comparatively high molecular weight, and a preparation process utilizing the catalyst composition.

SOLUTION: The propylene oxide polymerization catalyst composition comprises (1) a crown ether compound, (2) an alkali metal alkoxide or an alkali metal hydroxide, and (3) an organic Lewis acid in which all linkages are directly metal-bound carbon linkages not through an oxygen. A process for preparing a poly(propylene oxide) uses this polymerization catalyst composition in polymerizing propylene oxide to obtain the poly(propylene oxide).

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**CLAIMS**


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## [Claim(s)]

[Claim 1] (1) a crown-ether compound, (2) alkali-metal alkoxide or an alkali-metal hydroxide, and (3) -- the polymerization-catalyst constituent of the propylene oxide which includes the organic Lewis acid all the combination of whose is combination which carbon has combined with the metal through oxygen

[Claim 2] (1) A crown-ether compound is (2) alkali-metal alkoxide or an alkali-metal hydroxide. Polymerization-catalyst constituent of the propylene oxide according to claim 1 used one mols or more to one mol.

[Claim 3] (1) The polymerization-catalyst constituent of the propylene oxide according to claim 1 or 2 which is one sort chosen from the group which a crown-ether compound becomes from 18-crown -6, benzo 18-crown -6, dibenzo 18-crown -6, and dicyclohexano-18-crown-6, or two sorts or more.

[Claim 4] (3) The polymerization-catalyst constituent of a propylene oxide given in the claim 1 whose organic Lewis acid is one sort chosen from the group which consists of alkylaluminum, aryl aluminum, and alkyl aryl aluminum, or two sorts or more, or any 1 term of 3.

[Claim 5] (3) There is no claim 1 whose organic Lewis acid is one sort chosen from the group which consists of triisobutylaluminum, a triethylaluminum, a trimethylaluminum, triphenyl aluminum, diphenyl monochrome isobutyl aluminum, and monochrome phenyl diisobutyl aluminum, or two sorts or more, and it is the polymerization-catalyst constituent of a propylene oxide given in thing any 1 term.

[Claim 6] The poly (propylene oxide) manufacture method characterized by facing carrying out the polymerization of the propylene oxide and obtaining poly (propylene oxide), and using the polymerization-catalyst constituent of a publication for a claim 1 or any 1 term of 5 as a polymerization-catalyst constituent.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the polymerization-catalyst constituent of a propylene oxide, and the poly (propylene oxide) manufacture method. It is related with the polymerization-catalyst constituent and the manufacture method of manufacturing poly (propylene oxide) which has still more detailed comparatively high molecular weight.

[0002]

[Description of the Prior Art] Even if it polymerization-makes the polymerization of the propylene oxide hard to carry out as compared with ethylene oxide, the molecular weight of product polymer has many comparatively low things, and cannot carry out control of molecular weight further easily, either. Then, research is advanced focusing on the initiator and the catalyst to obtain the polymer of the amount of macromolecules moreover, controlling the molecular weight of the polymer obtained. By the method using a Lewis acid and a phosphonium halogenide, there is a report to which the polymerization of the propylene oxide could be carried out until now. By this method, the polymer which has a hydroxyl group at the end cannot be obtained, and it may not be suitable for a resin raw material. Moreover, there is a report to which the polymerization of the propylene oxide could be carried out by the method using an aluminum porphyrin. By this method, in order to use the aluminum porphyrin which it is comparatively expensive and is hard to come to hand in large quantities, there was a field it cannot be said that is industrial. Then, controlling the molecular weight of the product obtained, the product of high molecular weight was obtained and, moreover, it waited for development of the practical manufacture method on industry.

[0003]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the manufacture method using the polymerization-catalyst constituent and its catalyst constituent of the propylene oxide which can control the molecular weight of polymer, is made to generate poly (propylene oxide) which has a hydroxyl group at the end with moreover comparatively high molecular weight, and can do things.

[0004]

[Means for Solving the Problem] When this invention persons faced carrying out the polymerization of the propylene oxide and obtaining poly (propylene oxide), as a result of inquiring wholeheartedly that the above-mentioned technical problem should be solved and the special polymerization-catalyst constituent was used, the polymerization of a pre pyrene oxide was made very good, and moreover they find out that the molecular weight is a macromolecule comparatively, and came to complete this invention.

[0005] namely, this invention -- (1) crown-ether compound, (2) alkali-metal alkoxide or an alkali-metal hydroxide, and (3) -- all combination offers the polymerization-catalyst constituent of the propylene oxide which includes the organic Lewis acid which is combination which carbon has combined with the metal through oxygen. Moreover, for this invention, (1) crown-ether compound is (2) alkali-metal alkoxide or an alkali-metal hydroxide. The polymerization-catalyst constituent of the aforementioned propylene oxide used one mols or more is offered to one mol. Furthermore, this invention offers the polymerization-catalyst constituent of the aforementioned propylene oxide which is one sort chosen from the group which (1) crown-ether compound becomes from 18-crown-6, benzo 18-crown-6, dibenzo 18-crown-6, and dicyclohexano-18-crown-6, or two sorts or more. this invention offers the polymerization-catalyst constituent of the aforementioned propylene oxide whose (3) organic Lewis acid is one sort chosen from the group which consists of alkylaluminum, aryl aluminum, and alkyl aryl aluminum, or two sorts or more further again. Moreover, this invention offers the polymerization-catalyst constituent of the aforementioned

propylene oxide whose (3) organic Lewis acid is one sort chosen from the group which consists of triisobutylaluminum, a triethylaluminum, a trimethylaluminum, triphenyl aluminum, diphenyl monochrome isobutyl aluminum, and monochrome phenyl diisobutyl aluminum, or two sorts or more. Furthermore, this invention is faced carrying out the polymerization of the propylene oxide and obtaining poly (propylene oxide), and the poly (propylene oxide) manufacture method characterized by using the aforementioned polymerization-catalyst constituent as a polymerization-catalyst constituent is offered.

[0006]

[Embodiments of the Invention] this invention -- the polymerization of a propylene oxide -- facing -- (1) crown-ether compound, (2) alkali-metal alkoxide or an alkali-metal hydroxide, and (3) All combination uses the polymerization-catalyst constituent which makes a principal component the organic Lewis acid which is combination which carbon has combined with the metal through oxygen.

[0007] (1) It is an annular polyether and the whole ring serves as a multidentate ligand by electron-donative oxygen, and a crown-ether compound will not be limited especially if it has the function to incorporate the ion of alkali metal in hole of a ring. As these compounds, 18-crown -6, benzo 18-crown -6, benzo 15-crown -5, dibenzo 18-crown -6, dibenzo 18-crown -3, dibenzo 24-crown -8, dibenzo 30-crown -10, dicyclohexano-18-crown-6, dicyclohexano-24-crown-8, etc. can be mentioned. Especially, it is 18-crown. - 6, benzo 18-crown -6, dibenzo 18-crown -6, dicyclohexano-18-crown-6 It can use preferably. Moreover, (1) crown-ether compound can also use two or more sorts together if needed.

[0008] (2) An alkali-metal alkoxide or especially an alkali-metal hydroxide does not limit the kind. For example, as an alkali-metal alkoxide, methoxides, such as caesium, a rubidium, a potassium, sodium, and a lithium, ethoxide, propoxide, butoxide, etc. can be mentioned. Especially, it is a potassium. As an alkali-metal hydroxide which can be used especially preferably, t-butoxide can mention a lithium hydroxide, a sodium hydroxide, a potassium hydroxide, a cesium hydroxide, a hydroxylation rubidium, etc., for example. A potassium hydroxide can be used especially preferably. [0009] (3) An organic Lewis acid is aluminum or the compound complex of boron preferably that what is necessary is just the organic metal which has a ligand (as far as it is related with the organic Lewis acid of this specification still at least, a "metal" is caught in a wide sense and also describes boron as a metal). The alkyl aryl machine which the aforementioned ligand has branching respectively independently, or can be the shape of a chain without branching, and an annular thing, and has the aryl group; aforementioned alkyl group and aryl groups of carbon numbers 6-20, such as an alkyl group; phenyl group of the carbon numbers 1-10, such as an isobutyl machine, and a naphthyl group; it can be those derivatives and it is important that all combination with a ligand and a metal is combination which carbon and the metal have combined through oxygen. As such a compound, triisobutylaluminum, a triethylaluminum, a trimethylaluminum, triphenyl aluminum, diphenyl monochrome isobutyl aluminum, monochrome phenyl diisobutyl aluminum, triphenyl boron, TORI (pentafluorophenyl) boron, etc. are mentioned, for example. The compound containing aluminum is desirable and triisobutylaluminum can be used especially preferably. Moreover, (3) organic Lewis acid can also use two or more sorts together if needed.

[0010] The polymerization of the propylene oxide using the polymerization-catalyst constituent of this invention can be performed by the same method as the case where other well-known catalysts are used. For example, (1) crown-ether compound is dissolved in a suitable solvent, and (2) alkali-metal alkoxide or an alkali-metal hydroxide is added, and is made to react. Subsequently, the polymerization of the propylene oxide of an initial complement is added and carried out to the solution which added and obtained (3) organic Lewis acid further.

[0011] (1) As for a crown-ether compound, it is desirable to use one mols or more to (2) alkali-metal alkoxide or one mol of alkali-metal hydroxides. A reaction rate falls in less than one mol. (3) As for an organic Lewis acid, it is desirable to use one mols or more to (2) alkali-metal hydroxide or one mol of alkali-metal alkoxides. In less than one mol, a reaction does not progress in many cases. In one mols or more, the polymerization reaction of a propylene oxide becomes quick, so that many. Moreover, the amount of (3) organic Lewis acid used to a propylene oxide is 2 - 5% especially preferably 1 to 8% still more preferably 0.1 to 10% preferably in the mole ratio of a metal atom (for example, aluminum atom) to a propylene oxide. There is an inclination for a reaction rate to become it slow that it is less than 2%, and a reaction may be unable to progress easily at less than 1%.

[0012] Although the mechanism of the polymerization-catalyst constituent of this invention is not clear, a crown-ether compound carries out the inclusion of the alkali-metal ion, and the metal atom contained in an organic Lewis acid is considered to be because for arrangement effective in

carrying out the polymerization of the propylene oxide to be taken. Therefore, the poly (propylene oxide) molecular weight obtained is controllable by adjusting the mole ratio of (2) alkali-metal alkoxide, or an alkali-metal hydroxide and a propylene oxide.

[0013] The well-known thing used for the polymerization of a propylene oxide can be used for the solvent to be used. For example, they can be ether, aliphatic hydrocarbon, aromatic hydrocarbons, halogen system solvents (methylene chloride etc.), and ketones. Especially if reaction temperature is general temperature, it cannot be limited, but it can be the same temperature requirement as the conventional case. However, 0-50 degrees C is desirable. Moreover, arbitrary well-known additives can be used in the range which does not check a reaction.

[0014] Poly (propylene oxide) obtained by this invention is applicable to various uses. For example, it can use as adhesives, an urethane raw material and a resin raw material, a surfactant raw material, etc.

[0015]

[Example] Hereafter, although an example explains this invention further, it does not come to limit this invention to these examples. In addition, the "section" in an example is based on a weight. Moreover, the reaction was performed under inert gas and non-water atmosphere. The molecular weight and molecular weight distributions Mw (weight average molecular weight)/Mn (number average molecular weight) of a product sampled the reactant, added methano 1 RU of optimum dose, evaporated it, remelted the generated polypropylene oxide to the tetrahydrofuran (THF), and measured it by GPC (for tetrahydrofurans) after filtration with the Teflon filter. The yield of a reaction also samples a reactant. It computed from the result of 1 H-NMR. [0016]

Example 1 KOH The 2mmol, the 18-crown-6 2mmol, and the 4mmol (aluminum<sub>3</sub> (i-Bu)) mol of triisobutylaluminum were melted to 1 and 2-dimethoxyethane, and volume was set to 20ml. That is, concentration of K<sup>+</sup> was carried out in 0.1 mols/l. Next, 1ml was taken for this solution (the 0.1mmol of KOH(s), a 18-crown-6 0.1mmol, and aluminum(i-Bu)<sub>3</sub> 0.2mmol), and the 2mmol (it is 2ml about an one mol [l. ] hexane solution) was added for aluminum (i-Bu)<sub>3</sub> there. and toluene -- 10ml -- adding -- diluting -- a propylene oxide -- a 100mmol -- in addition, at the room temperature, it stirred for 5 hours and the polymerization was carried out A result is shown in Table 1. In addition, the hydroxyl values of this resultant were 12.8 mg-KOH per [ which was generated ] polypropylene-oxide 1g. It investigated about poly (propylene oxide) the monomer conversion ratio, number average molecular weight (Mn), and molecular weight distribution (Mw/Mn) which were obtained. A result is shown in Table 1.

[0017] examples 2-6 -- the example 1 was repeated except having changed again, as an aluminium compound and reaction time were indicated to Table 1 A result is shown in Table 1.

[0018] In addition, a part of used aluminium compound was obtained by the following methods. Triphenyl aluminum: 8.0g (33mmol) of refined triphenyl boron was put into the flask, subsequently, 50ml of dryness toluene was added and 38ml (triethylaluminum 36mmol) of triethylaluminum 0.94 mol/l hexane solutions was further added to this. This mixture was heated and 50ml (it mainly consists of a hexane) of solvents was distilled off. After that It heated flowing back a solvent (it mainly consisting of toluene). This heating reflux was performed for 5 hours. After cooling the obtained reaction mixture to a room temperature, it decompressed with the vacuum pump and toluene was evaporated nearly completely. The obtained reaction mixture was heated at 150 degrees C under reduced pressure for 3 hours. The generated triethyl boron is removed by this reduced pressure operation. The obtained reaction mixture solidified, when it cooled to the room temperature, although it was in the melting state. This solid-state was set to toluene 20ml the dissolution and \*\* exception, and hexane 40ml was added, it crystallized, and the crystal of triphenyl aluminum was obtained. The crystal was taken out and what carried out reduced pressure drying was used for this example after washing by the hexane. In addition, yield was 4.2g (49% of yield).

Diphenyl monochrome isobutyl aluminum: Triphenyl aluminum 4mmol and triisobutylaluminum 2mmol were dissolved in toluene 20ml, and it heated under toluene reflux for 1 hour. It was used for this example, having used this reactant as diphenyl monochrome isobutyl aluminum.

Monochrome phenyl diisobutyl aluminum: Triphenyl aluminum 2mmol and triisobutylaluminum 4mmol were dissolved in toluene 20ml, and it heated under toluene reflux for 1 hour. It was used for this example, having used this reactant as monochrome FENIRUJI iso butyl aluminum.

[0019]

[Table 1]

Example Organic Lewis acid Monomer conversion ratio . Mn (Mw/Mn) Polymerization time 1 aluminum<sub>3</sub> (i-Bu) 100% 10200 (1.5) 5 hours 2 AlEt<sub>3</sub> 82% 2800 (1.6) 24 hours 3 AlMe<sub>3</sub> 51% 1100 (1.5) 24 hours 4 AlPh<sub>3</sub> 64% 3600 (1.7) 24 hours 5 AlPh<sub>2</sub> (i-Bu) 100% 7300 (1.6) 8 hours 6 AlPh(i-Bu)<sub>2</sub> 100% 8000 (1.6) 8 hours. [0020] the inside of the above-mentioned table 1, and

AlEt<sub>3</sub> a triethylaluminum -- meaning -- AlMe<sub>3</sub> a trimethylaluminum -- meaning -- AlPh<sub>3</sub> meaning triphenyl aluminum, AlPh<sub>2</sub> (i-Bu) means diphenyl monochrome isobutyl aluminum -- AlPh (i-Bu)<sub>2</sub> Monochrome phenyl diisobutyl aluminum is meant.

[0021]

[Effect of the Invention] According to this invention, the molecular weight of polymer can be controlled and the manufacture method using the polymerization-catalyst constituent and its catalyst constituent of the propylene oxide which is made to generate poly (propylene oxide) which has a hydroxyl group at the end with moreover comparatively high molecular weight, and can do things is offered.

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[Translation done.]